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Enterprise ionic liquids database (ILUAM) for its use in Aspen ONE programs suite with COSMO-based property methods

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Abstract

An enterprise database of pure ionic liquids (ILs) for its use in the Aspen ONE programs is presented. The database is identified as ILUAM and the first version (ILUAM01) contains 100 ILs composed by 30 cations and 23 anions. The IL components were introduced in Aspen Properties as pseudocomponents using information from the computational COSMO-RS method and from experimental viscosity data. ILUAM database was created for its use along with the COSMOSAC property model implemented in Aspen Plus, allowing evaluating IL process performance without needing further experimental data. Some validation tests were carried out to demonstrate the successful incorporation of ILs in the Aspen Plus property system. Then, the performance of ILUAM01 database in thermodynamic property predictions of mixtures involving ILs and conventional chemical compounds was revised in terms of activity coefficients at infinite dilution and phase equilibrium data. The property description of pure ILs and IL mixtures with conventional chemical compounds using COSMO-based/Aspen Plus approach was found with the accuracy level required in the conceptual design of new processes. ILUAM database offers the opportunity of performing systematic evaluation of potential industrial applications of ILs and their competitiveness as alternative to conventional solvents.

Keywords: Ionic liquids, Process simulation, Aspen ONE, Enterprise database, COSMO-methodologies.

1. Introduction

Ionic liquids, with remarkable physicochemical and solvent properties, have powerfully attracted the attention of the scientific community as potential alternative to organic solvents in industrial chemical processes[1,2]. A main advantage of this class of compounds is that the cation and the anion can be selected among a huge diversity to obtain a proper IL for a specific purpose. Therefore, ILs are known as "designer solvents"[3,4]. However, the practical application to industrial processes of a large number of ionic liquids is as yet limited by different reasons[5,6] including that they are still expensive and some of them exhibit unfavorable transport properties. Thus, the future application of the ILs at industrial scale will be severely determined by the quality and robustness of the process developments that have to be made. This includes the technical soundness as well as the energetic and economic viability of the proposals[7,8].

In the scenario depicted above, process simulation could play a determinant role because its support to the synthesis and the analysis of the new processes comprising the use of ILs and, because it can contribute to conform multifactorial and consistent sets of criteria (thermodynamic, kinetic, technical, energetic and economic) for selecting the ILs with optimized properties for a specific application[9,10]. Nevertheless, modeling industrial processes with ILs using commercial process simulators is not a simple and straightforward question at all. Firstly, they are not conventionally included in the databases of these programs, but besides not enough experimental information is already available to do that for a significant number of these compounds. Secondly, using regressive thermodynamic models in property modeling is severely limited by the lack of experimental information noted before, to obtain the model parameters. This also happens with the predictive UNIFAC model (and other group contribution methods) for which, the available set of "conventional" groups and their corresponding parametrizations are not still sufficient for reproducing the structural and behavior diversity of the ILs. Thirdly, at the present, the favorable acceptance of the ILs as promising new components for industrial applications, demands massive system (solvents, reaction media, etc.) and process alternative evaluations. In this regard, a deep breakup between the information volume needed to evaluate the potential industrial applications of ILs and the current rhythm of the experimental data acquisition is observed. The massive character of these searches is mostly related to the designer nature of the ILs. The number of ions already explored for synthesizing ILs, yields a huge amount of compounds to be considered in the process analyses. But even more, the question is not limited to the number of ion combinations known at the present but it is also related to the increasing quantity of new cations and anions are being added continuously.

An affordable solution, at the current state of the art, is to combine predictive methods to estimate the properties of the ILs and their mixtures[11] with the process simulation[7]. This solution has been

addressed by several research groups in different application fields and using rather dissimilar strategies[7,12-19]. In particular, our group has been worked[20] in the integration of the molecular modeling and the process simulation via the COSMO-based[21,22] methods taking benefit from the two following individual issues: i) COSMO-RS/SAC models have been proved to be a valuable tool for predicting thermodynamic properties of mixtures composed by molecular solvents and ionic liquids[11,23] and even ionic liquid mixtures[24,25]; and ii) COSMO-type approaches have been implemented in Aspen Plus as property model, under the denomination of COSMOSAC, since its version 12.1[26]. More recently, thanks to the integrated approach incorporated in the Aspen ONE programs suite, the COSMOSAC property model can also be used in Aspen HYSYS by importing or selecting Aspen Properties fluid packages[27]. The COSMOSAC property model is actually the implementation of three different COSMO equations: i) the original COSMO-SAC model proposed by Lin and Sandler[22]; ii) the original COSMO-RS model proposed by Klamt[21]; and iii) the modification to the Lin and Sandler model developed by P. Mathias and coworkers[28]. By implicit, Aspen Plus uses the Lin and Sandler COSMO-SAC approach. The COSMO equation to be used can be selected by the user through the Option Codes in the Gamma calculations when the COSMOSAC property model is selected (Properties/Methods/Selected Methods). Codes 1 to 3 correspond, respectively, to the cited three models. For more details, see the Solution ID-37674 at the Aspen Tech Support Web page[29].

In the last five years, we have successfully applied COSMO-based/Aspen Plus (Aspen HYSYS) procedure to the design and analysis of new different processes using ILs: absorption of toluene in packed/tray columns[30], absorption refrigeration cycles[31], aromatic-aliphatic separation by liquid-liquid extraction[25,32,33], extractive distillation[34] and CO_2 capture by physical absorption[9]. In addition, the technical and economic impact of the solvent regeneration by distillation[8] in different processes was evaluated. From these works, three main results should be highlighted: i) COSMO-based/Aspen Plus (Aspen HYSYS) approach provides reasonably property predictions for ILs and their mixture with conventional chemical compounds[8,25,31,32]; ii) the competitiveness of the equipment designs reached[34] compared to those supported by regressive thermodynamic models like NRTL (which involves a previous fitting of the model parameters); and iii) the high capacity of the procedure to deal with multicomponent mixtures and complex process models[9,32,33].

In summary, it is technical and methodologically possible both to create non-database IL components and to specify the COSMOSAC property model, using solely the information generated by *a-priori* computational methods, in order to carry out process simulations and optimizations capable to solve the typical problems at the initial stages of the Process Engineering with adequate level of accuracy. However, doing that every time (for each individual process simulation) is a large-time consuming task and a clear source of errors by the data manipulation. For this reason, we

decided creating a pure component type Enterprise Database of ILs to be used with the programs of the Aspen ONE suite. Along with this, the COSMOSAC property model to calculate the activity coefficients of the components in a mixture was selected. This database was named ILUAM.

In this paper, the ILUAM database contents and its creation process are described. Details on the: i) compound identification and databank architecture, ii) IL pseudocomponent creation in Aspen Properties and COSMOSAC property model specification and, iii) computational and experimental data used in the database creation are provided. Furthermore, it was verified the correct incorporation of the ILs as new components in the Aspen Properties environment (database validation). For this, the values of some selected properties for the pure ILs were calculated by Aspen Plus simulations and compared to the experimental values obtained under the same operating conditions. In these simulations, IL components were selected from the ILUAM database after being properly registered as a new Aspen Physical Property Database in Aspen Properties. The properties tested were chosen according to their importance in the calculations corresponding to the Conceptual and Basic Engineering: density, surface tension, heat capacity and thermal conductivity. Later, the performance of the ILUAM01 database to describe the thermodynamic properties of mixtures including ILs and common chemical compounds was overviewed attending to available gas-liquid, vapor-liquid and liquid-liquid phase equilibrium data (654 points) and the activity coefficients at infinite dilution of 11 remarkably different solutes in ILs (780 points). Finally, a brief overview of the main contributions of COSMO-based/Aspen Plus (Aspen HYSYS) process simulations to the research on ILs, highlighting the potential application of ILUAM database to the development on new process based on ILs is presented, and the further developments of the ILUAM database are outlined.

2. Database description

2.1. Generalities.

The first version of the Enterprise Ionic Liquids Database (ILUAM01) contains 100 common ILs, composed by 30 cations and 23 anions with different structures (Table S1 to S3 in Supplementary Material). It has been created using information mainly obtained by *a priori* computational approaches based on COSMO and COSMO-RS methods. The database contains four separated databanks (Table 1) combining two different criteria: i) the molecular model used to describe the IL compounds in COSMO and COSMO-RS calculations. Ion pair (CA) and independent ions (C+A) structures have been considered[23] and, ii) the inclusion (or not) of the experimental viscosity-to-temperature dependence through Arrhenius equation[35] in the pseudocomponente especification. This improves the component definition in the case of rate-controlled operations. ID tags (CA) and (C+A) account for the molecular model to describe the IL components whereas EQ and RB labels

indicate the use of the corresponding databank appropriate for, respectively, equilibrium- or rate-controlled process simulations.

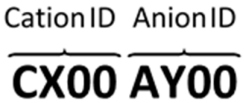
Table 1. Databanks included in the ILUAM01 database and their contents.

Databank Name	IL molecular model	Experimental viscosity
ILUAM01-(CA)-EQ	(CA)	No
ILUAM01-(C+A)-EQ	(C+A)	No
ILUAM01-(CA)-RB	(CA)	Yes
ILUAM01-(C+A)-RB	(C+A)	Yes

EQ-labeled databanks include only computational COSMO and COSMO-RS information for creating the IL pseudocomponents and, correspondingly, they are recommended only for equilibrium-controlled calculations. This databank is useful when IL viscosity-to-temperature experimental data is not available and it can be expanded to any new IL since only computational information obtained for molecular structure of IL is needed. RB-targeted ones contain the parameters of the Andrade´s equation following the Aspen Properties protocol, being suitable for rate-based calculations where the effect of the fluid transport properties is determinant[9,30].

2.2. IL identification

Creating a database of pure ILs for Aspen Properties entails a formal challenge related with the component identification. The IUPAC name of these compounds is, usually, very large and cannot be hosted in the 8-alphanumeric characters format used by Aspen Properties to identify the components. Alternative nomenclature employed with ILs is somewhat confuse and arbitrary and, finally, abbreviations used to designate them are not unique. Thus, the unequivocal identification of these components in the ILUAM01 database demanded an alternative solution. Each IL included in the current database has its own and characteristic ID, composed by 4 characters for the individual ions (cation and anion). The ID nomenclature is described in Scheme 1.



Scheme 1. IL identification in the ILUAM01 database.

The first letter indicates the cation (C) or the anion (A), the second character represents a general classification of the compound in different families (see Table 2), and the last two characters correspond to a hexadecimal number. Tables S1 and S2 of the Supplementary Material include the IDs of the 30 cations and 23 anions registered in the ILUAM01 database, with their name, common

abbreviations found in literature, family assignation according to Table 2, chemical structure and molecular weight. The identification information can also be read in Aspen Plus when both the components are selected and the stream compositions are specified.

Table 2. Ion identification in the ILUAM01 database

CATIONS		ANIONS	
ID	**Family**	**ID**	**Family**
1	Imidazolium	0	Halide
2	Pyridinium	1	Fluorinated
3	Pyrrolidinium	2	Carboxylate
4	Piperidinium	3	Metal
5	Ammonium	4	AHA
6	Phosphonium	5	CN-based
7	Sulfonium	6	P-based
8	Morpholinium	7	S-based
9	Quinolinium	8	Amino-acid
F	Other	F	Other

2.3. IL pseudocomponent creation and COSMOSAC property model specification

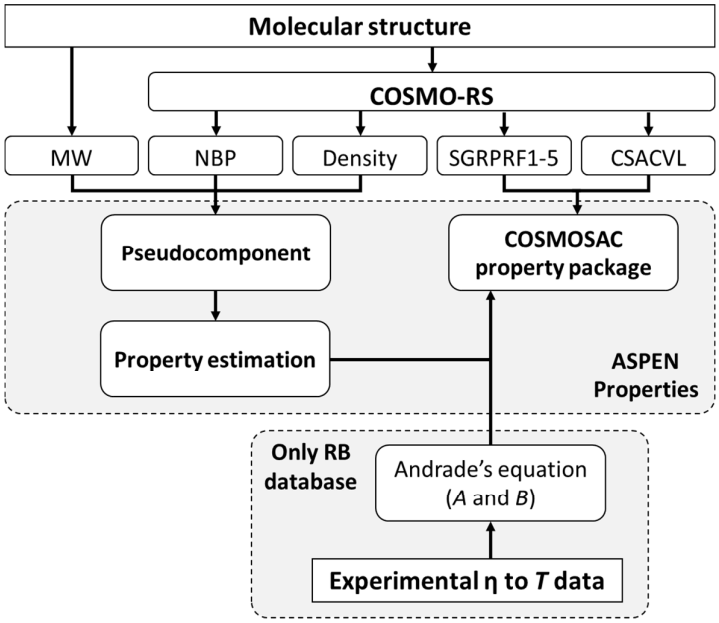
IL new components have been generated as pseudocomponents through Aspen Plus specifying their molecular weights, normal boiling temperatures (NBP) and densities (at 60 ºF). The remaining physical and thermodynamic properties, necessary to completely define the IL components, were estimated using the API-recommended procedures plus Aspen Physical Property System modifications (Aspen Tech and API procedures) as implemented by default in the Aspen Plus[36].

In order to support COSMOSAC property calculations[29], the information relative to the COSMO theory is added for every IL: the molecular volume and the sigma-profile[21,22]. Molecular volume is introduced as the scalar parameter CSACVL in the Aspen Property nomenclature. The sigma profile, which collects the polarized charge distribution in the molecule by the effect of its interaction with a continuous conductor, representing the solvent environment, is added as a five set of temperature-dependent parameters, designated SGPRF1 to SGPRF5 (see Figure S1), also according to the Aspen Property nomenclature.

Normal boiling temperatures, densities, molecular volumes and sigma-profiles were obtained by COSMO-RS calculations (see “Computational data” section). The ILUAM01-(CA)-RB and ILUAM01-(C+A)-RB databanks also include information on the experimental viscosity-to-temperature dependence, specified by using a two-parameters (Arrhenius type) Andrade´s equation fitted to available experimental data (see “Experimental data” section). Scheme 2 shows the information

flow used in this work to both create non-databank IL components and specify the COSMOSAC property model.

Scheme 2. Information flow used in both the IL pseudo-component creation and the COSMOSAC property model specification.



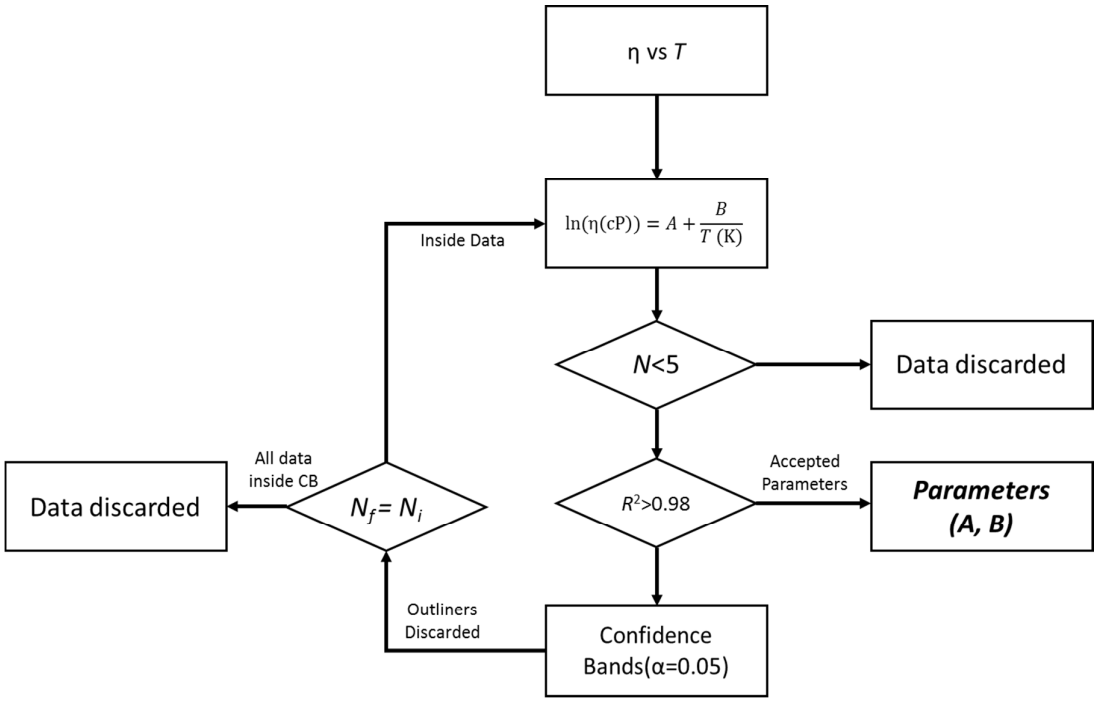
2.4. Computational data

The molecular geometries of the ionic pairs [(CA) models] and the corresponding individual ions [(C+A) models] were optimized at the BP86/TZVP computational level considering solvent interactions through the COSMO continuum solvation method[37]. Independent ions [(C+A) model] and ion pair [(CA) model] structures were optimized in our computational laboratory. Conformer with the lowest electronic energy was selected for each IL to be included in ILUAM01 database. Vibrational frequency calculations were performed in all the cases to confirm the presence of an energy minimum. The polarized charge distribution on the molecular surface was saved after optimization in a .cosmo file. All the quantum-chemical calculations as well as the .cosmo file generation were done using Turbomole 4.2 software[38]. COSMO*therm* program package version C30_1201[39] with BP_TZVP_C30_1201 parametrization was used to perform COSMO-RS calculations, obtaining the required NBP, density, molecular volume and the sigma-profile values in Scheme 2.

2.5. Experimental data

The experimental viscosity database for regressing the parameters (*A* and *B*) of the Andrade´s equation was obtained from the NIST Standard Reference Database #147 ILthermo. All the data collected were filtered prior to the statistical fitting in order to ensure information of liquid phase measurements in a pressure range between 50 and 150 kPa (almost atmospheric pressure). Viscosities for the whole temperature range available for each IL were taken. In order to obtain reliable viscosity-to-temperature data a statistical refining was done following the procedure described in Scheme 3[35].

Scheme 3. Methodology employed for statistical fitting and refining experimental viscosity data series



First, all data for each IL were fitted to Andrade´s equation reduced to two parameters (A and B), Arrhenius type, equation[35]. When fulfilling the two criteria of having 5 or more points (*N*) and R^2 equal to or greater than 0.98, the parameters A and B for the equation were saved. When R^2 was lower than 0.98, confidence bands (with α=0.05) were built and all the outliners were rejected (viscosity values discarded) from the data set and a new fitting with the "inside data" was done. In case that no outliners were discarded but R^2 remained below 0.98 (N_f = N_i), the adjustment could not be further improved, so the data set was discarded. This procedure was applied iteratively until the acceptation conditions were fulfilled or the data set was rejected. After refining a huge literature data set 2634 data points (taken from 198 references) were preserved and included in RB-

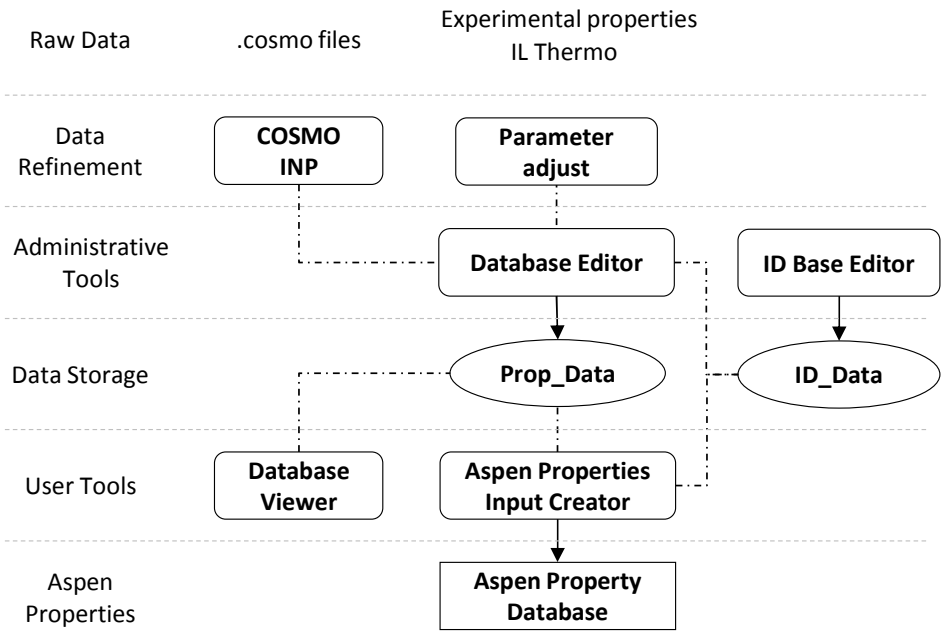
databanks of ILUAM01. Experimental data for other properties (density, surface tension, heat capacity and thermal conductivity) of pure ILs -used in this work for validating the adequate incorporation of the ILs, through ILUAM01 database, as components in Aspen ONE process simulators- were also collected (and adequately filtered) from the ILthermo Web page. The experimental database managed in this work is characterized in Table 3.

Table 3. Number of experimental data points/ILs/references included in ILUAM01 database validation.

Property	Experimental points	ILs	References
Density	8378	99	546
Heat Capacity	4132	59	68
Surface Tension	2257	71	100
Thermal Conductivity	318	33	11
Viscosity	3761	100	278

2.6. Database creation

An Excel VBA code to be used as helping complement for both the database developers and their final users was programmed attending the structure depicted in Scheme 4. In order to guarantee the unequivocal identification of the ILs and the unambiguous data assignation to each of them, *ID Base Editor* manager creates or edits the IDs for each ion present in the database and stores them in *ID_Data*. *COSMO INP* and *Parameter adjust* codes are in charge to the automatic or semi-automatic data generating and management. *Database Editor* code stores all the information gathered in the *Prop_Data* archive, allowing the creation of different property sets with different characteristics (such COSMO-RS parametrization, IL molecular model, etc.) and checks that the information provided is unique for each ID.



Scheme 4. Structure of the Excel VBA code used to generate ILUAM01.

An important feature of this program is its modular organization, which allows replacing, or modifying individual (for data storage) Excel books without affecting the overall functional structure of the code. On the other hand, these Excel books can contain more information than the one included in the Aspen Properties database which enables its further development.

Finally, using *Aspen Input Creator* code, a massive data transportation from the *Prop_Data* Excel was accomplished in order to collect the required information to create the new IL component. This code was used to create the four ILUAM01 databanks of Table 1, which were saved as individual .inp archives to be directly open as Aspen Plus database. Thus, for all the 100 ILs, the database constitutive items (MW, NBP, densities, molecular volumes and sigma-profile elements) were transported for defining EQ-labeled databanks. Additionally, Andrade´s equation parameters were transferred for RB-labeled databanks. The .inp files should be used to create the ILUAM01 database in Aspen Properties. As an additional tool, *Database Viewer* code of Scheme 4 allows the user both the correct component identification and the knowledge of the available information on it (see Figure 1).

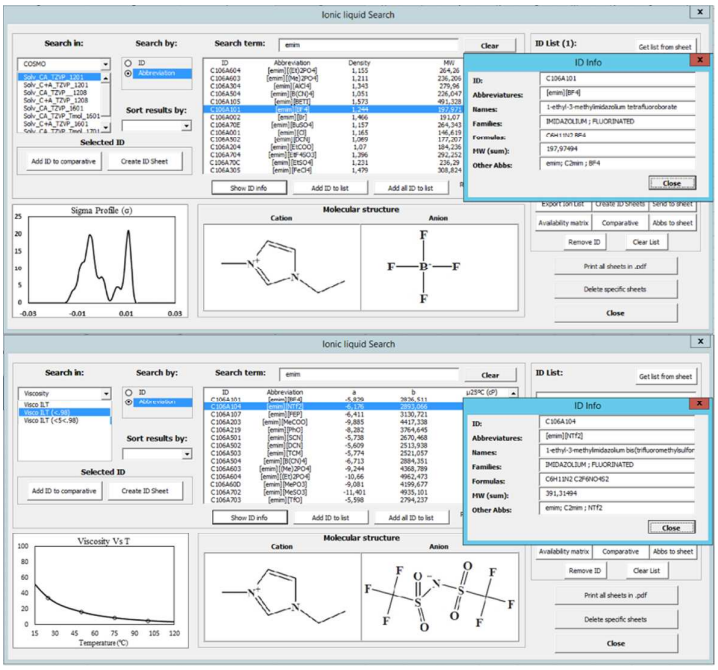


Figure 1. Screenshots showing some utilities implemented in the *Database Viewer* programmed in VBA as user complement for selection and property analysis of the IL components included in the ILUAM01 database.

This is an important feature for the final user, taking into account the difficulties related to the IL identification. In addition, the component selection may be conditioned by the previous understanding of the properties of pure IL included ILUAM01 database. For example, the earlier knowledge of the sigma profile of the component (which collects the polarized charge by the effect of a conductor, describing the chemical nature of IL and anticipating its behavior as component in a mixture) or an indicative value of certain property (a low viscosity value, for instance) can help the user to select a particular component before making any calculation.

Once IL compounds are incorporated in Aspen Plus codes using ILUAM .inp files, process simulations can be carried out. The thermodynamics of IL mixtures with conventional chemical compounds are computed using COSMOSAC property model. The remainder (thermo-physical and transport) properties are calculated by the computational procedures implemented in Aspen Plus by default. ILUAM database and all the associated information (manual, tutorial and representative test cases) is available in www.uam.es/Ciencias/ILUAM .

3. ILUAM01 database validation

In order to check the successful incorporation of the IL components in Aspen One process simulator through ILUAM01 database, simple simulations were carried out using Aspen Plus (v 9.1) to calculate thermo-physical and transport properties of the pure ILs. The properties tested were density, surface tension, heat capacity and thermal conductivity; all of them commonly used in process simulations corresponding to Conceptual and Basic Engineering. Regarding these properties, it should be remarked that their Aspen Plus calculations are merely predictive, since (unlike the viscosity) no experimental information was used. In the validations, the calculated values were compared to the available experimental data (see "Experimental data" section and Table 3) at atmospheric pressure and temperatures in the interval 298-373 K.

Table 4 summarizes the mean absolute percentage errors (MAPE, %) of the COSMO-based Aspen Plus predictions using the different ILUAM01 databanks at 298 K. Detailed data for each property is collected in Tables S4-S7 of the Supplementary Material. As can be seen, with independence of the computation approach used, errors are low for density, reasonable for heat capacity and thermal conductivity but somewhat elevated for surface tension. In this regard, it should be indicated that several authors[40,41] reported the remarkable experimental dispersion of available data for heat capacity and, particularly, thermal conductivity and surface tension of ionic liquids, due to sample impurity and other factors. In the particular case of the surface tension, it should also be considered that the model used by default in Aspen Plus has shown low predictability for common chemical compounds as discussed elsewhere[42]. On the other hand, small differences were observed when using (CA) and (C+A) molecular models to describe the IL compound (Table 4), being obtained that (CA) model provides more accurate predictions of pure IL properties, with the exception of the surface tension. As expected, introducing experimental viscosity-to-temperature dependence in IL component definition (RB databanks) does not affect the predictions of density, heat capacity, surface tension and thermal conductivity, since the property models used to describe these properties do not depend on viscosity. Table 4 also includes the viscosity estimations of ILs by COSMO-based/Aspen Plus approach using EQ-based databanks. The unacceptable error obtained demonstrates the needed of using experimental-based viscosity definition included in RB-labeled databanks when ILUAM01 is used in rate-controlled operations.

Table 4. Mean absolute percentage error of property predictions for pure ILs in ILUAM01 database using COSMO-based/Aspen Plus Approach at 298 K.

	Mean Absolute Percentage Error (%)				
ILUAM01 Databank	**Density (*N*=99)[a]**	**Heat capacity (*N*=59)[a]**	**Thermal conductivity (*N*=33)[a]**	**Surface tension (*N*=71)[a]**	**Viscosity (*N*=100)[a]**
(CA)-EQ	1.6	13.7	12.8	57.3	$8 \cdot 10^{14}$
(CA)-RB	1.6	13.7	12.8	57.3	-

(C+A)-EQ	1.7	19.2	13.4	51.1	$4 \cdot 10^9$
(C+A)-RB	1.7	19.2	13.4	51.1	-

[a] N: number of used experimental data

Figure 2 compares the experimental and calculated property values of pure of ILs at 298 K obtained with COSMO-based/Aspen Plus approach using ILUAM01-(CA)-EQ databank. For density and heat capacity, the different families of ILs with common anion follow a similar trend (linear regression of calculated-experimental data close to 1), observing higher dispersion for heat capacity values, in concordance with the higher mean absolute error of Table 4. In the case of thermal conductivity, higher dispersion is observed, particularly for the cases of ILs with anion based on cyano functional group ([DCN]$^-$, for instance) which are clearly overestimated. As expected, the data dispersion for surface tension is high and no clear experimental-calculated linear relationship is found, obtaining high mean absolute errors (Table 4).

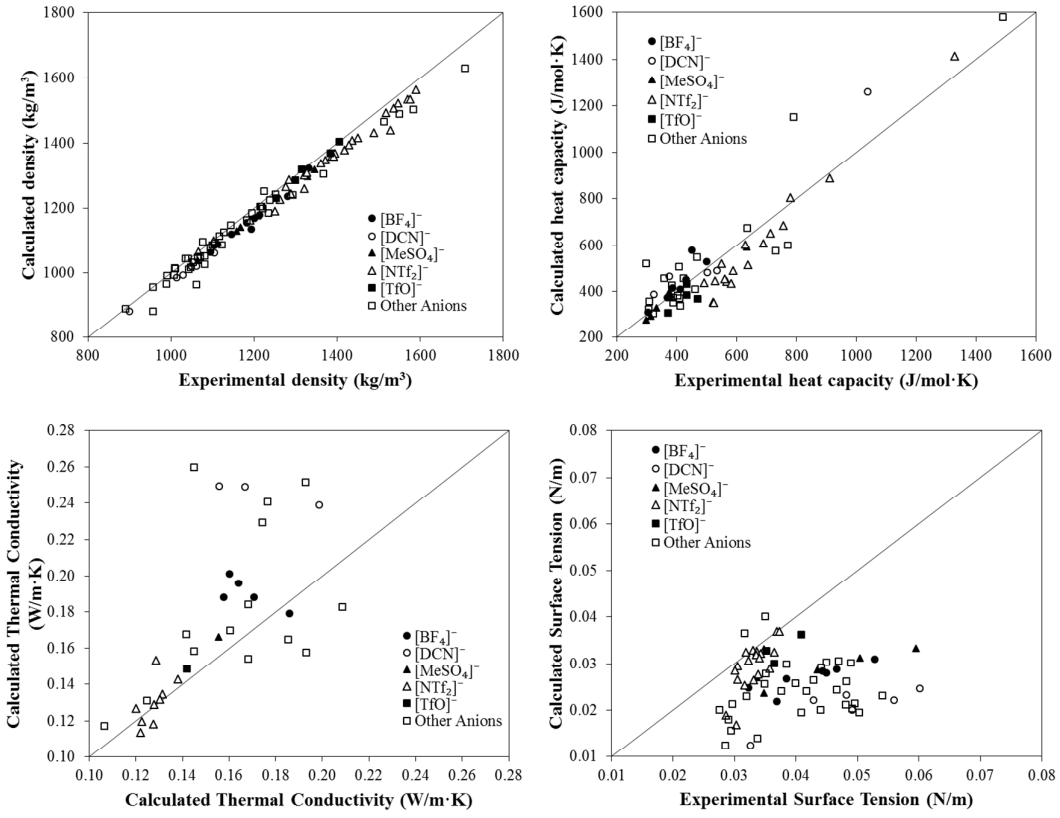


Figure 2. Comparison of experimental property values of IL at 298 K to those calculated by COSMO-based/Aspen Plus approach using ILUAM01-(CA)-EQ databank.

Figure 3 presents the MAPE values of IL property values calculated by COSMO-based/Aspen Plus approach using ILUAM01-(CA)-EQ databank in function of temperature (273-373 K), being observed that the accuracy of COSMO-based/Aspen Plus predictions is not strongly affected by temperature.

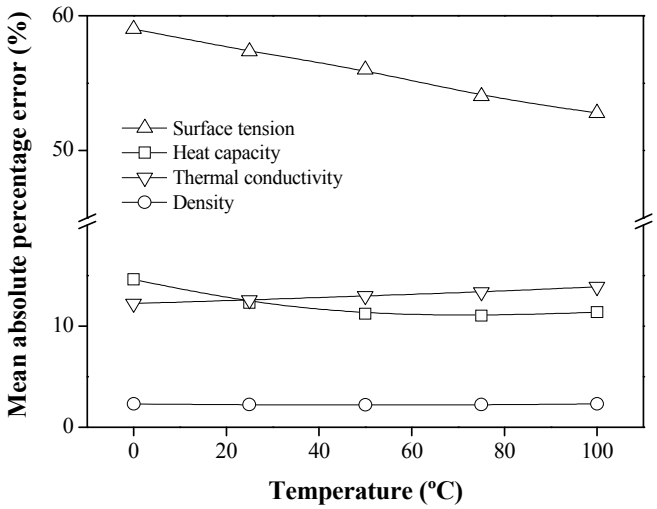


Figure 3. Mean absolute percentage errors of COSMO-based/Aspen property predictions using ILUAM01-(CA)-EQ in function of operating temperature.

In sum, the validation performed demonstrates that the ILUAM01 database (including four databanks) can be successfully used in Aspen Plus, obtaining a description of the pure IL components with adequate level of accuracy to be used in simulations for the conceptual design of new processes based on ILs. This conclusion can be extended to Aspen HYSYS calculations, where the database ILUAM01 and the COSMOSAC model can be selected from the Aspen Property system thanks to its integration at the Aspen ONE suite.

The performance of COSMO-based/Aspen Plus (Aspen HYSYS) methodology to describe the thermodynamic behavior of multiphasic systems involving ILs and conventional chemical compounds has been evaluated in previous works[8,9,25,30-34]. The obtained predictability of COSMO-based/Aspen Plus (Aspen HYSYS) approach for phase equilibrium data of IL mixtures is illustrated in Table 5, including gas-liquid (GLE), vapor-liquid (VLE) and liquid-liquid (LLE) cases. It is observed that this computational approach provides reasonably property predictions for ILs and their mixture with conventional chemical compounds, at least with the level of accuracy required for first stage of process development. As can be seen, the obtained mean absolute percentage error (MAPE) depends on both the type of phase equilibrium system and the molecular model used to describe

the ILs [VLE: 13% (CA), 22% (C+A); LLE: 11% (CA), 21% (C+A); GLE: 24% (CA)], in general obtaining

Application	Reference	Components	Phase	Temperature (K)	N	MAPE (%) CA model	MAPE (%) C+A model
Regeneration of IL by distillation	8,33,34	Water/[emim][NTf_2]	VLE	353.15	6	7.5	2.2
		Methanol/[emim][$EtSO_4$]	VLE	303.15	14	1.8	6.8
		Methanol/[hxmim][NTf_2]	VLE	303.15	30	4.5	19.5
		Methanol/[mmim][Me_2PO_4]	VLE	303.15	28	12.4	7.6
		Ethanol/[emim][NTf_2]	VLE	343.15	28	16.0	28.9
		Ethanol/[hxmim][NTf_2]	VLE	343.15	28	16.4	35.2
		2-propanol/[bmim][NTf_2]	VLE	353.15	32	11.3	24.8
		2-propanol/[emim][NTf_2]	VLE	353.15	35	21.0	34.7
		Acetone/[bmim][NTf_2]	VLE	353.15	31	2.4	19.7
		Acetone/[emim][NTf_2]	VLE	353.15	29	15.9	26.5

better results with ion-pair structures (CA) than with independent ions (C+A) model.

		THF/[emim][NTf_2]	VLE	313.15	37	34.9	34.9
		Thiophene/[bmim][PF_6]	VLE	353.15	4	18.7	19.4
		Benzene/[bmim][PF_6]	VLE	-	7	6.9	25.8
		Benzene/[bmim][NTf_2]	VLE	-	38	5.4	-
		Benzene/[emim][NTf_2]	VLE	-	38	5.2	18.8
		Benzene/[mmim][NTf_2]	VLE	-	35	19.7	22.7
Aliphatic-aromatic separation by liquid-liquid extraction using IL	32-34	Heptane/Toluene/[emim][NTf_2]	LLE	298.15	10	6.5	-
		Hexane/Benzene/[emim][NTf_2]	LLE	298.15	9	21.0	-
		Hexane/Benzene/[emim][NTf_2]	LLE	313.15	9	21.5	-
		Hexane/Benzene/[bmim][NTf_2]	LLE	298.15	12	9.3	-
		Hexane/Benzene/[omim][NTf_2]	LLE	298.15	9	10.0	-
		Heptane/Toluene/[emim][TfO]	LLE	313.20	14	2.8	-
		Heptane/Toluene/[4mbpy][BF_4]	LLE	313.20	14	10.1	-
		Heptane/Toluene/[4mbpy][BF_4]	LLE	348.20	13	6.5	-
		Hexane/Benzene/[4mbpy][BF_4]	LLE	313.20	8	12.3	-
		Hexane/Benzene/[4mbpy][BF_4]	LLE	333.20	8	11.0	-
		Octane/Ethylbenzene/[4mbpy][BF_4]	LLE	313.20	8	8.8	-
CO_2 capture by physical absorption with IL	9	CO_2/[bmim][BF_4]	GLE	282-348	36	26.5	-
		CO_2/[bmim][PF_6]	GLE	283-348	36	36.9	-
		CO_2/[hxmim][NTf_2]	GLE	281-348	36	15.9	-
		CO_2/[hxmim][FEP]	GLE	298-343	12	18.2	-

Table 5. Mean absolute percentage error of phase equilibrium data for IL mixtures predicted by COSMO-based/Aspen Plus approach.

In order to perform a wider evaluation of COSMO-based/Aspen Plus (Aspen HYSYS) performance to describe the thermodynamics of IL mixtures, Figure 4 compares the experimental (from ILthermo database) and predicted values (780 data points) of activity coefficient at infinite dilution (γ_i^{∞}) of 11 representative chemical compounds (benzene, toluene, heptane, 1-heptene, dibutyl ether, pyridine, formaldehyde, acetone, acetic acid and water) in several ionic liquids (21) at different temperature (293-373 K), for the case of using ILUAM01-(CA)-EQ databank and COSMO-SAC equation (Code 1) of COSMOSAC property model (see Figure S2 in Supplementary Material for other cases). Table 5 collects the results of statistical analysis from fitting calculated to experimental γ_i^{∞} values, using different molecular models and COSMO-based equation of COSMOSAC property model. As can be seen, COSMO-based/Aspen Plus (Aspen HYSYS) approach predicts reasonably - without using experimental data- the thermodynamic behavior of mixtures including ILs, describing as positive as negative deviations from ideality and also ideal behaviors. Even when the average error of predicted activity coefficient of γ_i^{∞}at infinite dilution (Table 6) are larger than those error found for GLE, VLE and LLE data of real IL mixtures (Table 5), COSMO-based/Aspen Plus (Aspen HYSYS) methodology successfully describes the effect of the chemical nature of the components on IL mixture properties, fact of great interest in the selection of IL as adequate solvent is new chemical processes.

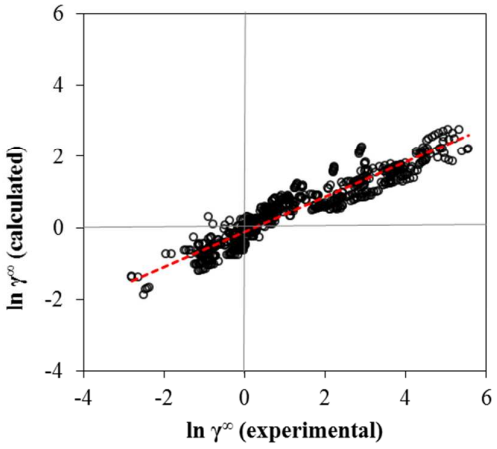


Figure 4. Activity coefficient at infinite dilution (γ_i^{∞}) of conventional chemical compounds in ionic liquids at 293-373 K temperature range predicted by COSMO-based/Aspen Plus methodology using ILUAM01-(CA)-EQ databank and COSMO-SAC equation (Code 1) of COSMOSAC property model.

Table 6. Statistical results from comparing experimental and calculated $ln\gamma_i^{\infty}$ values (780 data points) of 11 solutes in 21 ILs at 293-373 K temperature range by using ILUAM databanks in COSMO-based/Aspen Plus approach.

		Linear regression			
Equation	**IL model**	**Slope**	**Intercept**	**R^2**	**MAPE (%)**
COSMOSAC (Code 1)	CA	0.49	-0.10	0.892	45,5
COSMO-RS (Code 2)	CA	0.32	-0.34	0.850	57,4
Mathias (Code 3)	CA	0.44	-0.17	0.911	50,6
COSMOSAC (Code 1)	C+A	0.70	0.087	0.845	51,9
COSMO-RS (Code 2)	C+A	0.44	-0.256	0.816	50,8
Mathias (Code 3)	C+A	0.62	-0.053	0.870	44,2

4. ILUAM01 scope

As we noted, COSMO-based/Aspen Plus (Aspen HYSYS) approach has been already successfully applied to the study of several processes involving ILs, mainly centered on separations of mixtures. Simulations were performed without problems of consistency related IL incorporation as pseudocomponent. Furthermore, using COSMOSAC property model allows describing the thermodynamics of the mixtures with ILs without calculation errors. As a result, COSMO-based/Aspen Plus (Aspen HYSYS) simulations were perform to design individual operation units (mixers/splitters, separator, exchangers, pressure changers, columns, etc.) with systems including ILs using the available models in Aspen ONE process simulators[8,32-33]. Moreover, several individual operations units were successfully integrated in complex process based on ILs, what necessarily include recycles to reuse the IL solvent[9,33,34]. Once the process modeled, sensitivity analysis and

optimization of the operating variables can be performed, attending to chemical or energy consumes or operating and capital costs[9,33]. As remarkable advantage, COSMO-based Aspen Plus/Aspen HYSYS calculations can manage with multicomponent mixtures since it is an *a priori* approach. ILs were evaluated as separating phase in complex aromatic-aliphatic separation processes involving naphtha feed with realistic composition[32-34] or CO_2 capture processes for treating postcombustion fuel gas[9]. Even, it has been possible to evaluate the potential advantages of using mixtures of ILs as solvents by using current approach[25,32].

From previous studies, some noticeable contributions of using COSMO-supported Aspen Plus simulations in the research on new applications of ILs are: i) evaluating the performance of ILs as solvent in the process at industrial scale using models for commercial equipment; ii) introducing additional criteria to select the adequate ILs for an specific application, expanding the design of the solvent to role of the physicochemical, thermodynamic and kinetic properties of the system in the process performance; and iii) carrying out viability analysis of the new process based on IL by comparison to the results obtained with available technologies using conventional solvents. It should be emphasized that such previous studies were always done including a limited number of ILs, mainly selected attending to their separation capacity. ILUAM01 database offers the opportunity of performing systematic evaluation of potential industrial applications of ILs, providing a general perspective of cation-anion role in process performance and the competitiveness of IL as alternative to conventional solvents.

5. Further developments

Once the logistic necessary for the data base creation has been proved and the database validated, different development directions will be explored: i) adding new ILs to the database; ii) improving the IL definition by the inclusion of new properties; iii) using other advanced regressive methods -such as artificial neural networks- in the case of those properties (as surface tension) for which predictive methods do not ensure good estimations and; iv) using the different available COSMOtherm parametrizations to perform COSMO-RS calculations. In this sense, user individual requests can be considered under agreement.

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7. Supporting information

A Supplementary Material is additionally provided as support of this paper. Its contents are conveniently presented along the text. This material is available free of charge via Internet at: http://pubs.acs.org/.

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